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Improved treatment of momentum at classically forbidden electronic transitions in trajectory surface hopping calculations

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Abstract

We present a new prescription (called the ∇V prescription) for treating classically forbidden surface hops in semiclassical trajectory surface hopping simulations. The new method uses gradient information about the target electronic surface to determine the nuclear dynamics at a frustrated hopping event. We have tested this prescription, along with previously suggested prescriptions, against accurate quantum dynamics for 21 cases. We find that the fewest switches with time uncertainty (FSTU) algorithm with the ∇V prescription for momentum changes at frustrated hops is the most accurate of the six variants of the surface hopping approach that we tested.

1. Introduction

Electronically nonadiabatic chemical dynamics (e.g., nonadiabatic charge transfer, ultraviolet photodissociation, chemiluminescence, etc.) is described by coupled potential energy surfaces, and the applicability of fully converged quantum mechanical calculations is limited by computational considerations to systems with two atoms or three atoms and a few electronic states. It is desirable, therefore, to develop and validate the accuracy of approximate methods that may be applied to the large class of chemically interesting electronically nonadiabatic systems for which quantum mechanical calculations are not currently computationally feasible.

We have recently undertaken a program of developing realistic coupled potential energy surfaces for model three-atom reactive systems, performing fully three-dimensional accurate quantum calculations on the model systems, and systematically testing semiclassical methods against the accurate quantum calculations [1–7]. We have focused on semiclassical methods that are well defined so that they are systematically testable, computationally straightforward to implement, and readily applicable to large systems. Specifically, we have focused on methods that are based on what may be called the 'trajectory ensemble' or TE approach [8], where the nuclear wave packet is approximated as an ensemble of noninteracting classical trajectories.

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Of course, classical trajectories do not exhibit quantum effects (such as transitions between electronic states, tunneling, etc.), and when these effects are important, they must be explicitly added to the TE simulation. The key quantum effect for electronically nonadiabatic processes is the nonadiabatic transition itself, and a careful treatment of quantum transitions between electronic states is crucial in accurately modeling the dynamics of electronically nonadiabatic systems. The trajectory surface hopping [1–15] (TSH) approach starts from the TE formalism and includes nonadiabatic dynamics by allowing the trajectories in the ensemble to suddenly switch (i.e., to hop between) electronic states. The present Letter is primarily concerned with the treatment of the nuclear momentum at so-called frustrated hopping points along the classical trajectory in the TSH method.

2. Theory

Briefly, the TSH method is implemented as follows. One first chooses an electronic representation with which to express the electronic energies and the electronic-state coupling. The potential energy surfaces for a nonadiabatic chemical system may be chosen either as the unique set of adiabatic potential energy surfaces, coupled by the nuclear momentum and nuclear kinetic energy operators and corresponding to electronic wave functions that are eigenfunctions of the electronic Hamiltonian, or as a nonunique set of diabatic potential energy surfaces, for which the nuclear momentum coupling and nuclear kinetic energy coupling is small compared to a scalar (potential energy) coupling introduced by the adiabatic–diabatic transformation. (Sometimes diabatic states are called 'quasidiabatic' to emphasize that, in general, except for the trivial case of frozen electronic wave functions, a diabatic representation whose nuclear momentum couplings are exactly zero does not exist for real chemical systems [8,16,17]). Quantum mechanically, diabatic representations and the adiabatic representations obtained by diagonalizing the potential energy result in identical dynamics. TSH simulations, however, are sensitive to the choice of electronic representation, and we have determined [5] that the best representation to use is the one with the least amount of nonadiabatic coupling as measured by the number of attempted surface hops. This best representation (called the Calaveras County or CC representation) may be estimated from a small batch of TSH trajectories run in both representations.

Once an electronic representation is chosen, each trajectory in the ensemble is assigned an initial electronic state that corresponds to the initial conditions of the simulation. For example, if the quenching of an excited electronic state is being modeled, all of the trajectories start in the excited electronic state. The initial coordinates and momenta of each trajectory are selected randomly from a quasiclassical distribution [18], such that the initial ensemble of positions and momenta mimics the initial quantum mechanical wave packet. Each trajectory is then propagated classically (i.e., using Hamilton's equations of motion) under the influence of the potential energy surface that corresponds to the initial electronic state.

At arbitrarily small time intervals (such as the time step of the integrator), an electronic transition (or hopping) probability g_{ij} from the currently occupied electronic state i to some other target electronic state j is computed according to Tully's fewest-switches (TFS) algorithm [12,15]. The fewest-switches hopping probability is a function of the quantum mechanical electronic state populations, which are obtained by integrating the electronic Schrödinger equation along the classical trajectory. When this particular choice for the hopping probability is used, the TSH method is called the TFS method. A random number is generated and compared with g_{ij} to determine if a surface hop occurs. If a surface hop does not occur, the trajectory remains in the currently occupied electronic state. If a hop is called for, an electronic state change occurs, and the trajectory is propagated under the influence of the potential energy surface corresponding to the new electronic state.

Each trajectory in the ensemble may be thought of as an energy-conserving gas-phase event. When a surface hop occurs, the potential energy, in general, changes discontinuously, and the total energy of the system is conserved by adjusting the nuclear momentum. It has been suggested on the

basis of semiclassical arguments [11,13] and confirmed with numerical tests against accurate quantum dynamics [1,2] that the best way to conserve energy is to adjust the nuclear momentum component in the direction of the hopping vector **h**, where **h** is a unit vector in the direction of the nuclear momentum coupling vector **d**. Whether or not a hop occurs, the trajectory is propagated forward one time step where another hopping decision is made, etc..., and the process is continued until the trajectory is deemed 'finished' by some criterion (usually the separation of the products).

Occasionally, a surface hop to a higher-energy electronic state is called for at a point along the trajectory where the energy gap between the occupied and the target electronic states is greater than the kinetic energy associated with the momentum along **h**. When this occurs, the momentum cannot be adjusted along **h** in such a way as to conserve total energy, and these failed hopping attempts are called 'frustrated' or 'classically forbidden' surface hops [6,7].

Previous treatments for frustrated hopping include ignoring the frustrated hop [14] or reflecting the nuclear momentum along **h** as though the trajectory hits a barrier as it tries to hop, and we will denote these two approaches with a '+' and a '−', respectively (e.g., the TFS+ and TFS− methods employ the same surface hopping algorithm, but differ in their treatment of frustrated hopping). In both cases, the trajectory continues without changing electronic states, which violates the self-consistency argument originally used to justify the TFS algorithm [12]. Numerical studies [6,7] of these methods have shown that the resulting electronic-state distribution of trajectories results in increased errors. (We note that Tully's original implementation of the TFS method was the TFS− method [19]. We also note that in some work both criteria have been used depending on other details of the frustrated hop [3,10], or the momentum was changed along directions other than **h** [3,4,6], but we have found [3,4,6] that such methods do not improve the accuracy compared to the simple + and − prescriptions.)

We have recently developed [7] a new implementation of the TSH method called the fewest switches with time uncertainty (FSTU) method which allows a trajectory that experiences a frustrated hop to hop nonlocally to a geometry along the trajectory where a hop is classically allowed so long as the nonlocal hopping point is within a time interval obtained from the time–energy Heisenberg uncertainty relations. (In other respects, the FSTU method is the same as the TFS algorithm.) By introducing nonlocal hopping, the FSTU method improves the electronic-state distribution of trajectories, and the FSTU method was found [7] to be more accurate than the TFS method. Although the FSTU method has less frustrated hopping than the TFS method, not all frustrated hops are removed, and therefore we have previously considered [7] two implementations of the FSTU method, namely FSTU+ and FSTU−.

From numerical studies [6,7], we found that, in general, the TFS+ and FSTU+ methods are more accurate in predicting the average rotational and vibrational quantum numbers than are the TFS− and FSTU− methods, respectively, whereas the TFS− and FSTU− methods predict more accurate nonadiabatic transition probabilities and branching ratios. It is therefore reasonable to attempt to combine these two approaches. We note that a previous attempt [10] to combine the + and − approaches was unsuccessful because it relied on a nonphysical criterion for discriminating between the + and − treatments. In particular, the criterion was based on the amount of energy in modes orthogonal to **h** at a frustrated hop.

A new physically motivated prescription, called the ∇V prescription, is presented here that combines the desirable features of the + and − treatments in a more physically motivated fashion while retaining the simple implementation of the TSH method. Using the ∇V prescription, the dynamics at a frustrated hopping event is determined by allowing the trajectory to instantaneously feel the target electronic state. Specifically, when a frustrated hop is encountered, the following quantities are computed:

$$p_{\mathbf{h}} = \mathbf{p} \cdot \mathbf{h}, \tag{1}$$

$$F_{\mathbf{h}} = -\nabla \mathrm{V}_j \cdot \mathbf{h}, \tag{2}$$

where **p** is the nuclear momentum of the trajectory and ∇V_j is the gradient of the target electronic state j. Eqs. (1) and (2) are the projection of the nuclear momentum and the force of the target electronic state along the hopping vector **h**, respectively. If these two quantities have the same sign, the target electronic state can be thought of as instantaneously accelerating the trajectory along **h**, whereas if the two quantities have opposite signs, the target electronic state instantly retards the trajectory along **h**. We therefore use the following criterion for frustrated hopping

$$\text{If } p_{\mathbf{h}}F_{\mathbf{h}}\begin{cases}\geqslant 0 & \text{the } + \text{ treatment is used,}\\ < 0 & \text{the } - \text{ treatment is used.}\end{cases} \tag{3}$$

The ∇V criterion has several desirable features: it contains both + and − treatments, it is simple to implement, it requires only information that is readily available in surface hopping computer codes, it is physical as it depends only on the components of the momentum along the hopping vector **h** to determine the nonadiabatic dynamics, and it incorporates a knowledge of the character of the excited surface to differentiate whether the + or − treatment is used.

3. Calculations

We tested the FSTU∇V, FSTU+, and FSTU− methods against accurate quantum mechanical results for a total of 21 test cases involving fully three-dimensional collisions of systems with realistic potential energy surfaces. Four parameterizations of the YRH system [6] with three different sets of initial conditions for the Y*+RH collision partners and three parameterizations of the MXH system [20] with three different sets of initial conditions for the M* + XH collision partners were included in the test set. In both cases, an asterisk denotes electronic excitation. Descriptions of the surfaces, the initial conditions, and the quantum mechanical calculations for the YRH and MXH surfaces have appeared previously [6,20]. The entire set of 21 test cases is qualitatively diverse and use of such a diverse set of test cases ensures against fortuitous agreement between the semiclassical and quantum mechanical results. The CC electronic representation was used for all of the semiclassical calculations.

Unsigned relative errors (UREs) were computed for eight observables: the reactive de-excitation probability P_R to produce R + YH or H + MX, the nonreactive de-excitation (quenching) probability P_Q to produce Y + RH or M + XH, the total de-excitation probability $P_N = P_R + P_Q$, the product branching fraction $F_R = P_R/P_N$, the averages (first moments) of the final reactive vibrational and rotational quantum numbers v' and j', and the averages (first moments) of the final quenching vibrational and rotational quantum numbers v'' and j''. Note that all reactive events are electronically nonadiabatic; electronically excited channels of R + YH or H + MX are not energetically accessible.

4. Results and discussion

For each of the eight observables, the UREs were averaged over all 12 YRH cases, all 9 MXH cases, and all 21 cases, and the resulting mean unsigned relative errors (MUREs) are summarized in Table 1. The average MURE for the four moments, the four probabilities, and all eight observables are also shown for each method in the last three columns of Table 1. The method with the lowest MURE is shown in bold for each case. Uncertainties in the MUREs were computed using the Monte Carlo uncertainties in the calculated observables (these uncertainties result from finite sampling of initial collision variables such as vibrational phase and rotational orientation). If another method has an MURE that is statistically indistinguishable (within a 1σ range) from the method with the lowest MURE, that method is also listed in bold, and all bold entries are considered as 'statistically significant winners.' Table 1 shows that treatment of the nuclear momentum at frustrated hops has a significant effect on the reactive probability P_R and the product branching fraction F_R. For both the YRH and MXH systems, the FSTU∇V method is more accurate than the FSTU+ and FSTU− methods for P_R and F_R. For P_Q and P_N, all three methods are statistically indistinguishable for both the YRH and MXH

Table 1
Mean unsigned relative errors (MUREs) for the 12 YRH cases, the 9 MXH cases, and all 21 cases[a]

System	Method	P_R	$\langle v' \rangle$	$\langle j' \rangle$	P_Q	$\langle v'' \rangle$	$\langle j'' \rangle$	P_N	F_R	Moms[b]	Probs[c]	All[d]
YRH	FSTU+	1.25	**0.14**	**0.15**	**0.21**	**0.27**	**0.79**	**0.19**	1.12	**0.34**	0.69	0.51
	FSTU−	0.75	**0.20**	**0.14**	**0.22**	0.37	**0.88**	**0.18**	0.67	**0.40**	**0.46**	**0.43**
	FSTU∇V	**0.54**	**0.18**	**0.14**	**0.20**	**0.34**	**0.92**	**0.15**	**0.63**	**0.40**	**0.38**	**0.39**
MXH	FSTU+	1.09	**0.29**	**0.13**	**0.24**	**0.13**	**0.16**	**0.30**	0.66	**0.18**	0.58	0.38
	FSTU−	0.98	**0.27**	**0.13**	**0.23**	**0.14**	**0.16**	**0.29**	0.58	**0.17**	0.52	**0.35**
	FSTU∇V	**0.88**	**0.28**	**0.13**	**0.26**	**0.12**	**0.15**	**0.26**	**0.54**	**0.17**	**0.48**	**0.33**
Both[e]	FSTU+	1.18	**0.20**	**0.14**	**0.22**	**0.21**	**0.52**	**0.24**	0.92	**0.27**	0.64	0.46
	FSTU−	0.85	**0.23**	**0.13**	**0.23**	0.27	**0.57**	**0.23**	0.63	**0.30**	0.48	**0.39**
	FSTU∇V	**0.69**	**0.23**	**0.14**	**0.23**	**0.25**	**0.59**	**0.20**	**0.59**	**0.30**	**0.42**	**0.36**

[a] The methods with the statistically lowest MUREs for each observable are given in bold. See the text for more details.
[b] Average of the $\langle v' \rangle$, $\langle j' \rangle$, $\langle v'' \rangle$, and $\langle j'' \rangle$ MUREs.
[c] Average of the P_R, P_Q, P_N, and F_R MUREs.
[d] Average of all eight MUREs.
[e] MUREs averaged over all 21 test cases.

Table 2
Unsigned relative errors for the 12 YRH and 9 MXH cases

System	Initial conditions[a]	Parameterization[b]	P_N			F_R		
			FSTU+	FSTU−	FSTU∇V	FSTU+	FSTU−	FSTU∇V
YRH	(1.10, 0)	0.20	0.38	0.32	**0.14**	0.71	0.42	**0.10**
		0.10	**0.06**	**0.08**	0.17	0.57	0.30	**0.15**
		0.03	0.15	0.15	**0.05**	0.37	0.08	**0.07**
		0.01	**0.33**	**0.33**	**0.14**	**0.07**	**0.07**	**0.06**
	(1.10, 6)	0.20	**0.01**	0.09	**0.02**	0.54	**0.36**	0.60
		0.10	0.26	0.29	**0.24**	**0.66**	**0.67**	0.74
		0.03	**0.10**	**0.07**	**0.11**	**0.31**	0.39	0.46
		0.01	**0.11**	**0.07**	**0.13**	0.51	**0.40**	0.60
	(1.02, 0)	0.20	0.66	0.60	**0.45**	0.50	**0.00**	0.24
		0.10	**0.09**	0.13	0.18	3.58	2.37	**1.73**
		0.03	**0.05**	**0.03**	**0.05**	2.30	1.63	**1.18**
		0.01	**0.07**	**0.05**	**0.15**	3.26	**1.38**	1.57
Average of YRH cases			**0.19**	**0.18**	**0.15**	1.12	0.67	**0.63**
MXH	(1.10, 0)	SB	0.53	**0.44**	**0.43**	0.77	0.58	**0.48**
		SL	0.21	0.21	**0.18**	1.11	1.07	**1.00**
		WL	**0.35**	**0.34**	**0.31**	0.14	0.12	**0.08**
	(1.10, 1)	SB	0.19	**0.18**	**0.15**	1.45	0.99	**0.94**
		SL	0.18	0.19	**0.15**	1.46	1.42	**1.35**
		WL	**0.47**	**0.48**	**0.45**	0.19	0.17	**0.10**
	(1.10, 2)	SB	0.20	0.16	**0.12**	**0.23**	0.33	0.38
		SL	**0.40**	0.40	**0.37**	0.50	**0.45**	**0.43**
		WL	**0.19**	**0.19**	**0.18**	0.12	0.13	**0.08**
Average of MXH cases			**0.30**	**0.29**	**0.26**	0.66	0.58	**0.54**
Average of all 21 cases			**0.24**	**0.23**	**0.20**	0.92	0.63	**0.59**

[a] The initial conditions are denoted (E_{tot}/eV, j), where E_{tot} is the total energy in eV and j is the initial rotational state of the diatom. For more details see [6,20] for the YRH and MXH systems, respectively.
[b] See [6,20] for descriptions of the YRH and MXH parameterizations, respectively.

cases. The three methods predict all four MXH moments and three of the four YRH moments equally well. In the case of the quenching vibrational moment, the FSTU+ and FSTU∇V methods are statistically preferred over the FSTU− method for the YRH system.

Table 1 contains highly averaged errors over observables with varying magnitudes. Table 2 shows the UREs on a case-by-case basis for P_N and F_R and supports the conclusion drawn from Table 1 that the FSTU∇V method is the best method for F_R. Specifically, the FSTU∇V method has the statistically significant lowest URE for F_R for 14 of the 21 cases. We note that the trends in P_R are similar to the trends in F_R, and P_R is therefore not included in Table 2. Table 2 also reveals a trend in P_N that does not show up in the MUREs shown in Table 1. The FSTU∇V method has the statistically significant lowest URE for 19 of the 21 test cases for P_N. For the remaining two cases, the URE for all three methods is below 20%, where a 20% relative error may be considered satisfactory for semiclassical methods. We conclude therefore that the FSTU∇V method is better than the FSTU+ and FSTU− methods for P_N, P_R, and F_R.

In order to perform a case-by-case analysis on all eight of the observables without going into great detail, we have developed a scorecard method of evaluating the methods. In the scorecard method, for each of the eight observables a score of 1.0 is given to the statistically significant winning methods (as defined above), and a score of 0.0 is given to all other methods for that observable. The scores are then averaged over all 12 cases for YRH and all 9 cases for MXH. An average score of 1.0 or 0.0 indicates that the method predicts the statistically significant lowest unsigned error for all or none of the test cases, respectively. Table 3 shows these average scores for each observable. For each of the two kinds of systems (YRH and MXH), we averaged these average scores over all four probabilities, all four moments, and all eight observables, as shown in the last three columns of Table 3. Finally, we averaged over both kinds of systems, as shown in the last three rows. All averages are unweighted. Table 3 confirms the trends inferred from Tables 1 and 2, namely that the FSTU∇V method is greatly preferred over the other two methods in predicting probabilities (scoring 70% higher than the second-place method), that the FSTU+ method is preferred for predicting moments (scoring 22% higher than the second-place method), and that the FSTU∇V method is the best method overall (scoring 18% higher than the second-place method). Since there is no unique way to decide which method is 'better' over a diverse test set, we believe that it is encouraging that the mean unsigned relative errors and the

Table 3
Scorecard for the 12 YRH cases, the 9 MXH cases, and all 21 cases[a]

System	Method	P_R	$\langle v' \rangle$	$\langle j' \rangle$	P_Q	$\langle v'' \rangle$	$\langle j'' \rangle$	P_N	F_R	Moms[b]	Probs[c]	All[d]
YRH	FSTU+	0.33	0.92	0.92	0.83	1.00	0.67	0.67	0.25	0.88	0.52	0.70
	FSTU−	0.58	0.58	0.83	0.67	0.25	0.67	0.50	0.50	0.58	0.56	0.57
	FSTU∇V	0.67	0.75	0.83	0.83	0.25	0.42	0.83	0.50	0.56	0.71	0.64
MXH	FSTU+	0.11	0.78	0.78	0.56	0.67	0.89	0.44	0.11	0.78	0.31	0.54
	FSTU−	0.00	1.00	0.78	0.78	0.56	0.78	0.56	0.11	0.78	0.36	0.57
	FSTU∇V	0.89	0.78	0.89	0.67	0.44	1.00	1.00	0.89	0.78	0.86	0.82
Both[e]	FSTU+	0.22	0.85	0.85	0.69	0.83	0.78	0.56	0.18	0.83	0.41	0.62
	FSTU−	0.29	0.79	0.81	0.72	0.40	0.72	0.53	0.31	0.68	0.46	0.57
	FSTU∇V	0.78	0.76	0.86	0.75	0.35	0.71	0.92	0.69	0.67	0.78	0.73

[a] See Section 4 for a description of the scorecard method.
[b] Average of the $\langle v' \rangle$, $\langle j' \rangle$, $\langle v'' \rangle$, and $\langle j'' \rangle$ scores.
[c] Average of the P_R, P_Q, P_N, and F_R scores.
[d] Average of all eight scores.
[e] Average of the YRH and MXH scores.

scorecard method lead to the same conclusions. Furthermore, it is pleasing that the prescription that has the best physical justification also turns out to be the prescription that performs the most accurately.

We note that the FSTU∇V results in Tables 1 and 2 support our previous observation [6] that the semiclassical trajectory approach is reasonably accurate for modeling the dynamics of systems with weakly coupled electronic states. The YRH systems feature highly classically forbidden electronic transitions (the quantum mechanical values of P_N range from 0.2 to 10^{-4}), and the overall MURE of the improved semiclassical method (FSTU∇V) for these systems is 39%. For the more strongly coupled MXH systems (with quantum mechanical P_N from 0.5 to 0.7), the overall MURE is 33%. Considering the probabilities only, the FSTU∇V method performs better for the small-probability YRH cases than for the MXH cases, with average MUREs for the probabilities of 38% and 48%, respectively.

We also tested the TFS+, TFS−, and TFS∇V methods and obtained similar trends with respect to the treatment of frustrated hopping (i.e., the TFS∇V method is more accurate than the TFS+ and TFS− methods). We have previously shown [7] that the FSTU method is, in general, more accurate than the TFS method, and the same trends occur when both algorithms are implemented with the ∇V prescription, i.e., the FSTU∇V method has a smaller average error than the TFS∇V method. We also remind the reader that in previous papers [1–6], we have tested several other algorithms for treating surface hops, and this Letter results from a distillation of those efforts in that the methods presented here are only the very best methods.

5. Concluding remarks

The accuracy of semiclassical dynamics calculations using the trajectory surface hopping method for simulating non-Born–Oppenheimer processes is determined by the accuracy of the potential energy surfaces and the surface couplings, the selection of initial conditions, nonhopping trajectory propagation, the treatment of successful surface hops, and the treatment of frustrated hopping. We have shown in this work and previously [6,7] that frustrated hopping can be very important for realistic chemical systems, and allowing nonlocal hopping (as in the FSTU algorithm) and carefully treating frustrated hopping (as in the ∇V prescription) can have a significant quantitative effect on the overall semiclassical dynamics, and in some cases the treatment of frustrated surface hops is the dominant potential source of error. Semiclassical simulations of electronically nonadiabatic dynamics should therefore explicitly address the treatment of frustrated hopping, and based on the numerical studies presented here and elsewhere [6,7], we recommend the FSTU∇V method as the most successfully validated option for trajectory surface hopping calculations.

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